

Chemistry I: Gas Laws Notes

The Kinetic Molecular Theory of Ideal Gases

These statements are made only for what is called an ideal gas. They cannot all be rigorously applied (i.e. mathematically) to real gases, but can be used to explain their observed behavior qualitatively.

1. All matter is composed of tiny, discrete particles (molecules or atoms).
2. Ideal gases consist of small particles (molecules or atoms) that are far apart in comparison to their own size. The molecules of a gas are very small compared to the distances between them.
3. These particles are considered to be dimensionless points, which occupy zero volume. The volume of real gas molecules is assumed to be negligible for most purposes.

This above statement is NOT TRUE. Real gas molecules do occupy volume and it does have an impact on the behavior of the gas. This impact WILL BE IGNORED when discussing ideal gases.

4. These particles are in rapid, random, constant straight-line motion. Well-defined and established laws of motion can describe this motion.
5. There are no attractive forces between gas molecules or between molecules and the sides of the container with which they collide.

In a real gas, there actually is attraction between the molecules of a gas. Once again, this attraction WILL BE IGNORED when discussing ideal gases.

6. Molecules collide with one another and the sides of the container.
7. Energy can be transferred in collisions among molecules.
8. Energy is conserved in these collisions, although one molecule may gain energy at the expense of the other.
9. At any particular instant, the molecules in a given sample of gas do not all possess the same amount of energy. The average kinetic energy of all the molecules is proportional to the absolute temperature.

The Four Gas Law Variables: Temperature, Pressure, Volume, and Moles

I) Volume

All gases must be enclosed in a container that, if there are openings, can be sealed with no leaks. **The three-dimensional space enclosed by the container walls is called volume. When the generalized variable of volume is discussed, the symbol V is used.**

Volume in chemistry is usually measured in liters (symbol = L) or milliliters (symbol = mL). A liter is also called a cubic decimeter (dm^3).

Other units of volume do occur such as cubic feet (cu. ft. or ft^3) or cubic centimeters (cc or cm^3). **The main point to remember is: whatever units of volume are used, use them all the way through the problem. If you must convert from one unit to another, make sure you do it correctly.**

If the volume is constant, then the container is made with thick, rigid walls that cannot move. If the pressure increased too much, the walls would break, destroying the experiment. However, within the limits of any experiment discussed, the walls remain fixed and the volume stays constant

II) Temperature

All gases have a temperature, usually measured in degrees Celsius (symbol = $^{\circ}\text{C}$). Note that Celsius is capitalized since this was the name of a person (Anders Celsius). When the generalized variable of temperature is discussed, the symbol T is used.

There is another temperature scale, which is very important in gas behavior. It is called the Kelvin scale (symbol = K). Note that K does not have a degree sign and Kelvin is capitalized because this was a person's title (Lord Kelvin, his given name was William Thomson).

All gas law problems will be done with Kelvin temperatures. If you were to use degrees Celsius in any of your calculations, YOU WOULD BE WRONG.

You can convert between Celsius and Kelvin like this: Kelvin = Celsius + 273.15. The value of 273 is used instead of 273.15. For example, $25^{\circ}\text{C} = 298\text{ K}$, because $25 + 273 = 298$.

Standard temperature is defined as zero degrees Celsius or 273 K.

The Kelvin temperature of a gas is directly proportional to its kinetic energy. Double the Kelvin temperature, you double the kinetic energy.

III) Pressure

The molecules of gas hitting the walls of the container create gas pressure. This concept is very important in helping you to understand gas behavior. Keep it solidly in mind. This idea of gas molecules hitting the wall will be used often. When the generalized variable of pressure is discussed, the symbol P is used.

There are three different units of pressure used in chemistry. This is an unfortunate situation, but we cannot change it. You must be able to use all three. Here they are:

1. atmospheres (symbol = atm)
2. millimeters of mercury (symbol = mm Hg)
3. Torrs (symbol = torr)

You will find more pressure units on the reference sheet.

Standard pressure is defined as one atm. or 760.0 mm Hg or 760 torr.

Standard temperature and pressure is a very common phrase in chemistry, so common it has been abbreviated to **STP**. There is no such thing as standard volume, although you will probably learn about molar volume in your class.

IV. Amount of Gas

The amount of gas present is measured in moles (symbol = mol) or in grams (symbol = g). Typically, if grams are used, you will need to convert to moles at some point. When the generalized variable of amount in moles is discussed, the letter "n" is used as the symbol (note: the letter is in lowercase. The others above are all caps.).

Converting between Celsius and Kelvin

If you have a Celsius temperature in the problem, you MUST change it to Kelvin, in order to use it in your problem.

Sometimes your teacher might put a temperature in the problem, but you really don't need to use it

You can convert between Celsius and Kelvin like this: $\text{Kelvin} = \text{Celsius} + 273$. Often, the value of 273.0 is used instead of 273.15.

Essentially the 273 is being treated as 273.0

Converting between Units of Pressure: atm., mmHg and kPa

There are three different units of pressure used in chemistry. This is an unfortunate situation, but we cannot change it. You must be able to use all three. Here they are:

1. atmospheres (symbol = atm)
2. millimeters of mercury (symbol = mm Hg)
3. Torrs (symbol = torr)

Here is a repeat from each of the problem worksheets:

Abbreviations

atm - atmosphere

mm Hg - millimeters of mercury

torr - another name for mm Hg

K – Kelvin

°C - degrees Celsius

$$K = ^\circ C + 273$$

$$L \text{ (liter)} = 1000 \text{ mL}$$

Standard Conditions

$$0.00\text{ }^\circ\text{C} = 273\text{ K} \qquad 1.00\text{ atm} = 760.0\text{ mm Hg} = 760\text{ torr}$$

Boyle's Law

this law gives the relationship between pressure and volume if temperature and amount are held constant.

If the volume of a container is increased, the pressure decreases.

If the volume of a container is decreased, the pressure increases.

Explanation:

Suppose the volume is increased. This means gas molecules have farther to go and they will impact the container walls less often per unit time. This means the gas pressure will be less because there are less molecule impacts per unit time.

If the volume is decreased, the gas molecules have a shorter distance to go, thus striking the walls more often per unit time. This results in pressure being increased because there are more molecule impacts per unit time.

The mathematical form of Boyle's Law is: $PV = k$

This means that the pressure-volume product will always be the same value if the temperature and amount remain constant. This relationship was what Boyle discovered.

This is an inverse mathematical relationship. As one quantity goes up in the value, the other goes down.

Suppose P_1 and V_1 are a pressure-volume pair of data at the start of an experiment. In other words, some container of gas is created and the volume and pressure of that container is measured. Keep in mind that the amount of gas and the temperature DOES NOT CHANGE. When you multiply P and V together, you get a number that is called k . We don't care what the exact value is.

Now, if the volume is changed to a new value called V_2 , then the pressure will spontaneously change to P_2 . It will do so because the PV product must always equal k . The PV product CANNOT just change to any old value; it MUST go to k . (If the temperature and amount remain the same.)

So we know this: $P_1V_1 = k$

And we know that the second data pair equals the same constant: $P_2V_2 = k$

Since $k = k$, we can conclude that **$P_1V_1 = P_2V_2$** .

This equation of $P_1V_1 = P_2V_2$ will be very helpful in solving Boyle's Law problems.

Charles' Law

Discovered by Joseph Louis Gay-Lussac in 1802. He made reference in his paper to unpublished work done by Jacques Charles about 1787. Charles had found that oxygen, nitrogen, hydrogen, carbon dioxide, and air expand to the same extent over the same 80 degree interval.

This law gives the relationship between volume and temperature if pressure and amount are held constant.

If the volume of a container is increased, the temperature increases.

If the volume of a container is decreased, the temperature decreases.

Explanation:

Suppose the temperature is increased. This means gas molecules will move faster and they will impact the container walls more often. This means the gas pressure inside the container will increase (but only for an instant. Think of a short span of time. The greater pressure on the inside of the container walls will push them outward, thus increasing the volume. When this happens, the gas molecules will now have farther to go, thereby lowering the number of impacts and dropping the pressure back to its constant value.

It is important to note that this momentary increase in pressure lasts for only a very, very small fraction of a second. You would need a very fast, accurate pressure-sensing device to measure this momentary change.

Consider another case. Suppose the volume is suddenly increased. This will reduce the pressure, since molecules now have farther to go to impact the walls. However, this is not allowed by the law; the pressure must remain constant. Therefore, the temperature must go up, in order to get the molecules to the walls faster, thereby overcoming the longer distance and keeping the pressure constant.

Charles' Law is a direct mathematical relationship. This means there are two connected values and when one goes up, the other also goes up.

The mathematical form of Charles' Law is: $V \div T = k$

This means that the volume-temperature fraction will always be the same value if the pressure and amount remain constant.

Let V_1 and T_1 be a volume-temperature pair of data at the start of an experiment. If the volume is changed to a new value called V_2 , then the temperature must change to T_2 .

The new volume-temperature data pair will preserve the value of k . So we know this:
 $V_1 \div T_1 = k$

And we know this: $V_2 \div T_2 = k$

Since $k = k$, we can conclude that $V_1 \div T_1 = V_2 \div T_2$.

This equation of $V_1 \div T_1 = V_2 \div T_2$ will be very helpful in solving Charles' Law problems.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Notice that the right-hand equation results from cross-multiplying the first one. Some people remember one better than the other, so both are provided.

Before going to some sample problems, let's be very clear:

EVERY TEMPERATURE USED IN A GAS LAW CALCULATION MUST BE IN KELVINS, NOT DEGREES CELSIUS.

Gay-Lussac's Law

Discovered by Joseph Louis Gay-Lussac in the early 1800's.

Gives the relationship between pressure and temperature when volume and amount are held constant.

If the temperature of a container is increased, the pressure increases.

If the temperature of a container is decreased, the pressure decreases.

Gay-Lussac's Law is a direct mathematical relationship. This means there are two connected values and when one goes up, the other also increases.

The mathematical form of Gay-Lussac's Law is: $P \div T = k$

This means that the pressure-temperature fraction will always be the same value if the volume and amount remain constant.

Let P_1 and T_1 be a pressure-temperature pair of data at the start of an experiment. If the temperature is changed to a new value called T_2 , then the pressure will change to P_2 . Keep in mind that when volume is not discussed (as in this law), it is constant. That means a container with rigid walls.

As with the other laws, the exact value of k is unimportant in our context. It is important to know the PT data pairs obey a constant relationship, but it is not important for us what the exact value of the constant is. Besides which, the value of K would shift based on what pressure units (atm, mmHg, or kPa) you were using.

We know this: $P_1 \div T_1 = k$

And we know this: $P_2 \div T_2 = k$

Since $k = k$, we can conclude that $P_1 \div T_1 = P_2 \div T_2$.

This equation of $P_1 \div T_1 = P_2 \div T_2$ will be very helpful in solving Gay-Lussac's Law problems.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Notice the similarities to the Charles' Law formula. This is because both laws are direct relationships.

Make sure to convert any Celsius temperature to Kelvin before using it in your calculation.

Avogadro's Law

Discovered by Amedeo Avogadro, of Avogadro's Hypothesis fame. Gives the relationship between volume and amount when pressure and temperature are held constant.

Remember amount is measured in moles. Also, since volume is one of the variables, that means the container holding the gas is flexible in some way and can expand or contract.

If the amount of gas in a container is increased, the volume increases.
If the amount of gas in a container is decreased, the volume decreases.

Why?

Suppose the amount is increased. This means there are more gas molecules and this will increase the number of impacts on the container walls. This means the gas pressure inside the container will increase (for an instant), becoming greater than the pressure on the outside of the walls. This causes the walls to move outward. Since there is more wall space the impacts will lessen and the pressure will return to its original value.

The mathematical form of Avogadro's Law is: $V \div n = k$

This means that the volume-amount fraction will always be the same value if the pressure and temperature remain constant.

Let V_1 and n_1 be a volume-amount pair of data at the start of an experiment. If the amount is changed to a new value called n_2 , then the volume will change to V_2 .

We know this: $V_1 \div n_1 = k$

And we know this: $V_2 \div n_2 = k$

Since $k = k$, we can conclude that $V_1 \div n_1 = V_2 \div n_2$.

This equation of $V_1 \div n_1 = V_2 \div n_2$ will be very helpful in solving Avogadro's Law problems.

Here is the Law done up in fractional form, something HTML isn't good at:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Avogadro's Law is a direct mathematical relationship.

You prove Avogadro's Law every time you blow up a balloon.

Dalton's Law of Partial Pressures

This law was discovered by John Dalton in 1801.

For any pure gas (let's use helium), $PV = nRT$ holds true. Therefore, P is directly proportional to n if V and T remain constant. As n goes up, so would P . Or the reverse. Suppose you were to double the moles of helium gas present. What would happen?

Answer: the gas pressure doubles.

However, suppose the new quantity of gas added was a DIFFERENT gas. Suppose that, instead of helium, you added neon.

What would happen to the pressure?

Answer: the pressure doubles, same as before.

Dalton's Law immediately follows from this example since each gas is causing 50% of the pressure. Summing their two pressures gives the total pressure.

Written as an equation, it looks like this:

$$P_{\text{He}} + P_{\text{Ne}} = P_{\text{total}}$$

Dalton's Law of Partial Pressures: each gas in a mixture creates pressure as if the other gases were not present. The total pressure is the sum of the pressures created by the gases in the mixture.

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots + P_n$$

Where n is the total number of gases in the mixture.

The only necessity is that the two gases do not interact in some chemical fashion, such as reacting with each other.

The pressure each gas exerts in mixture is called its partial pressure.

The most common use of Dalton's Law seen in high school is with water vapor. A common method of collecting gas during an experiment is by trapping it "over water." An inverted bottle filled with water sits in a water bath. A tube from the reaction vessel conducts the gas into the bottle where it bubbles to the top and displaces water, which runs out the mouth of the bottle into the water bath.

However, there is an unavoidable problem. The gas saturates with water vapor and now the total pressure inside the bottle is the sum of two pressures - the gas itself and the added water vapor.

WE DO NOT WANT THE WATER VAPOR PRESSURE.

So we get rid of it by subtraction.

This means we must get the water vapor pressure from somewhere.

We get it from a table because the water vapor pressure depends only on the temperature, NOT how big the container is or the pressure of the other gas. Usually the textbook will have an abbreviated table with more complete tables in reference manuals like "The Handbook of Chemistry and Physics."

So finally, here is the example problem: 0.750 L of a gas is collected over water at 23.0°C with a total pressure of 99.75 kPa. What is the pressure of the dry gas? Look up the vapor pressure data on your reference sheet.

Combined Gas Law

To derive the Combined Gas Law, do the following:

Step 1: Write Boyle's Law:

$$P_1V_1 = P_2V_2$$

Step 2: Multiply by Charles Law:

$$P_1V_1^2 / T_1 = P_2V_2^2 / T_2$$

Step 3: Multiply by Gay-Lussac's Law:

$$P_1^2V_1^2 / T_1^2 = P_2^2V_2^2 / T_2^2$$

Step 4: Take the square root to get the combined gas law:

$$P_1V_1 / T_1 = P_2V_2 / T_2$$

If all six gas laws are included we would get the following:

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

However, this more complete combined gas law is rarely, if ever, discussed. Consequently, we will ignore it in future discussions and use only the law given in step 4 above.

Example #1: This type of combined gas law problem (where everything goes to STP) is VERY common:

2.00 L of a gas is collected at 25.0°C and 745.0 mmHg. What is the volume at STP?

STP is a common abbreviation for "standard temperature and pressure."

You have to recognize that five values are given in the problem and the sixth is an x.

Also, remember to change the Celsius temperatures to Kelvin.

Write a solution matrix, like this:

$P_1 =$	$P_2 = 760.0 \text{ mmHg}$
$V_1 =$	$V_2 = x$
$T_1 =$	$T_2 =$

and fill it in with data from the problem.

Here is the right-hand side filled in with the STP values:

$P_1 =$	$P_2 = 760.0 \text{ mmHg}$
$V_1 =$	$V_2 = x$
$T_1 =$	$T_2 = 273$

You can be pretty sure that the term "STP" will appear in the wording of at least one test question in your classroom. You should memorize the various standards conditions. If your teacher allows a reference to be used on the test, **MAKE CERTAIN** those values are there. Here's the solution matrix completely filled in:

$P_1 = 745.0 \text{ mmHg}$	$P_2 = 760.0 \text{ mmHg}$
$V_1 = 2.00 \text{ L}$	$V_2 = x$
$T_1 = 298 \text{ K}$	$T_2 = 273$

Insert the values in their proper places in the combined gas law equation and solve.

Example #2 - This next problem uses two gas laws in sequence. It involves using Dalton's Law of Partial Pressures first, then use of the Combined Gas Law. The explanation will assume you understand Dalton's Law. These two laws occurring together in a problem is VERY COMMON.

1.85 L of a gas is **collected over water** at 98.0 kPa and 22.0°C. What is the volume of the dry gas at STP?

The key phrase is "**over water**." Another phrase to look for is "wet gas." This means the gas was collected by bubbling it into an inverted bottle filled with water, which is sitting in a water bath. The gas bubbles in and is trapped. It displaces the water that flows out into the water bath.

The problem is that the trapped gas now has water vapor mixed in with it. This is a consequence of the technique and cannot be avoided. However, there is a calculation technique (Dalton's Law) that allows use to remove the effect of the water vapor and treat the gas as "dry." For this example, we write Dalton's Law like this:

$$P_{\text{gas}} + P_{\text{H}_2\text{O vapor}} = P_{\text{total}}$$

OR

$$P_{\text{gas}} = P_{\text{total}} - P_{\text{H}_2\text{O vapor}}$$

The vapor pressure of water at 22.0°C must be known and this data we must be taken from the reference source.

We solve the problem for P_{gas} and get 95.3553 kPa. Notice that it is not rounded off. The only rounding off done is at the FINAL answer, which this is not. Placing all the values into the solution matrix yields this:

$P_1=95.3553 \text{ kPa}$	$P_2=101.325 \text{ kPa}$
$V_1=1.85 \text{ L}$	$V_2=x$
$T_1=295 \text{ K}$	$T_2=273 \text{ K}$

Solve for x in the usual manner of cross-multiplying and dividing.

The Ideal Gas Law

An Ideal Gas is modeled on the Kinetic Theory of Gases which has 4 basic postulates:

- Gases consist of small particles (molecules) which are in continuous random motion
- The volume of the molecules present is negligible compared to the total volume occupied by the gas
- Intermolecular forces are negligible
- Pressure is due to the gas molecules colliding with the walls of the container

Real Gases deviate from Ideal Gas Behavior because:

- at low temperatures the gas molecules have less kinetic energy (move around less) so they *do* attract each other
- at high pressures the gas molecules are forced closer together so that the volume of the gas molecules becomes significant compared to the volume the gas occupies

Under ordinary conditions, deviations from Ideal Gas behavior are so slight that they can be neglected

A gas which deviates from Ideal Gas behavior is called a *non-ideal gas*.

PV = nRT: The Ideal Gas Law

For a static sample of gas, we can write each of the six gas laws as follows:

$$\begin{aligned}PV &= k_1 \\V / T &= k_2 \\P / T &= k_3 \\V / n &= k_4 \\P / n &= k_5 \\1 / nT &= 1 / k_6\end{aligned}$$

Note that the last law is written in reciprocal form. The subscripts on k indicate that six different values would be obtained.

When you multiply them all together, you get:

$$P^3V^3 / n^3T^3 = k_1k_2k_3k_4k_5 / k_6$$

Let the cube root of $k_1k_2k_3k_4k_5 / k_6$ be called R.

The units work out:

$$\begin{aligned}k_1 &= \text{atm-L} \\k_2 &= \text{L / K} \\k_3 &= \text{atm / K} \\k_4 &= \text{L / mol} \\k_5 &= \text{atm / mol} \\1 / k_6 &= 1 / \text{mol-K}\end{aligned}$$

Each unit occurs three times and the cube root yields L-atm / mol-K, the correct units for R when used in a gas law context.

$$\frac{PV}{nT} = R$$

Resuming, we have:

$$PV = nRT$$

or, more commonly:

R is called the gas constant. Sometimes it is referred to as the universal gas constant.

The Numerical Value for R

R values can be determined many ways. This is just one way:

We will assume we have 1.000 mol of a gas at STP. The volume of this amount of gas under the conditions of STP is known to a high degree of precision. We will use the value of 22.414 L.

By the way, 22.414 L at STP has a name. It is called molar volume. It is the volume of ANY ideal gas at standard temperature and pressure.

Let's plug our numbers into the equation:

$$(1.000 \text{ atm}) (22.414 \text{ L}) = (1.000 \text{ mol}) (R) (273.15 \text{ K})$$

Notice how atmospheres were used as well as the exact value for standard temperature.

Solving for R gives 0.08206 L atm / mol K, when rounded to four significant figures.

This is usually enough. Remember the value. You'll need it for problem solving.

Notice the weird unit on R: say out loud "liter atmospheres per mole Kelvin."

This is not the only value of R that can exist. It depends on which units you select.

Those of you that take more chemistry than high school level will meet up with 8.3145 Joules per mole Kelvin, but that's for another time. The ChemTeam will only use the 0.08206 value in gas-related problems.

Example #1 - A sample of dry gas weighing 2.1025 grams is found to occupy 2.850 L at 22.0°C and 740.0 mmHg. How many moles of the gas are present?

Notice that the units for pressure MUST be in atm., so the 740.0 mm Hg must be converted first.

$$740.0 \text{ mm Hg} \div 760.0 \text{ mm Hg/atm} = 0.9737 \text{ atm}$$

However, the unrounded-off value should be used in the calculation just below.

Now, plug into the equation:

$$(0.9737 \text{ atm}) (2.850 \text{ L}) = (n) (0.08206 \text{ L atm / mol K}) (295.0 \text{ K})$$

and solve for n.

Example #2 - Using the problem above, what is the molar mass of the gas?

This is a very common use of this law and the odds are very good you will see this type of question on a test.

The key is to remember the units on molar mass: grams per mole.

We know from the problem statement that 2.1025 grams of the gas is involved and we also know how many moles that is.

We know that from doing the calculation above and getting 0.1146 mol.

So all we have to do is divide the grams of gas by how many moles it is:

$$2.1025 \text{ g} \div 0.1146 \text{ mol} = 18.34 \text{ g/mol}$$

Let's go over those steps for using the Ideal Gas Law to calculate the molar mass of the gas:

- 1) You have to know the grams of gas involved. Usually the problem will just give you the value, but not always.
- 2) You are going to have to calculate the moles of gas. Use $PV = nRT$ and solve for n. Make sure to use L, atm and K.
- 3) Divide grams by moles and there's your answer.

Graham's Law

Consider samples of two different gases at the same Kelvin temperature.

Since temperature is proportional to the kinetic energy of the gas molecules, the kinetic energy (KE) of the two gas samples is also the same.

In equation form, we can write: $KE_1 = KE_2$

Since $KE = (1/2) mv^2$, (m = mass and v = velocity) we can write the following equation:

$$m_1 v_1^2 = m_2 v_2^2$$

Note that the value of one-half cancels.

The equation above can be rearranged algebraically into the following: the square root of $(m_1 / m_2) = v_2 / v_1$

A more practical way is:

R_a is the rate of gas a, R_b is the rate of gas b, MW_a is the molecular weight of gas a, and MW_b is the molecular weight of gas b.

$$\frac{R_a}{R_b} = \frac{\sqrt{MW_b}}{\sqrt{MW_a}}$$

You may wish to assure yourself of the correctness of this rearrangement. This last equation is the modern way of stating Graham's law.